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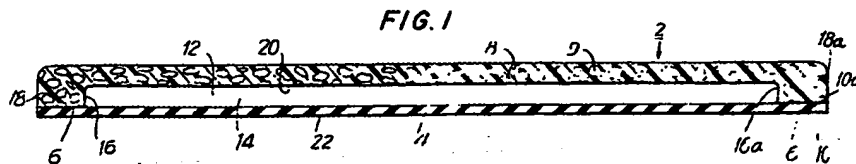
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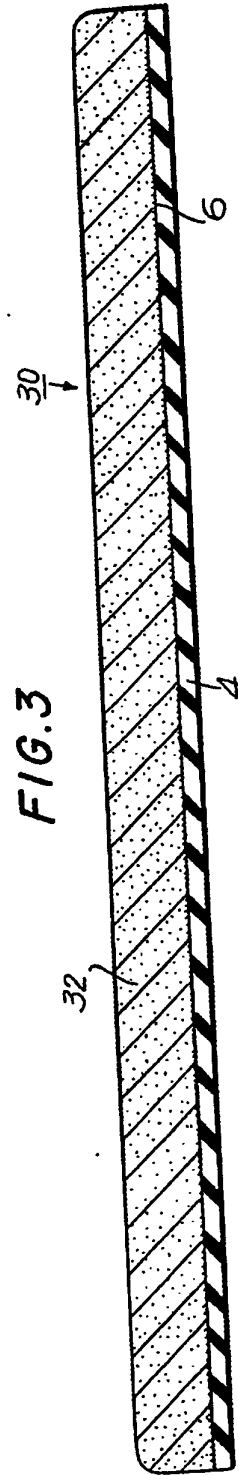
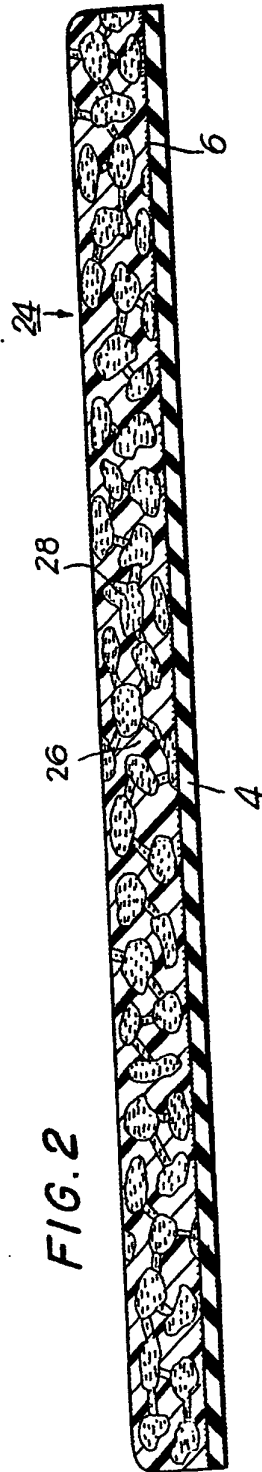
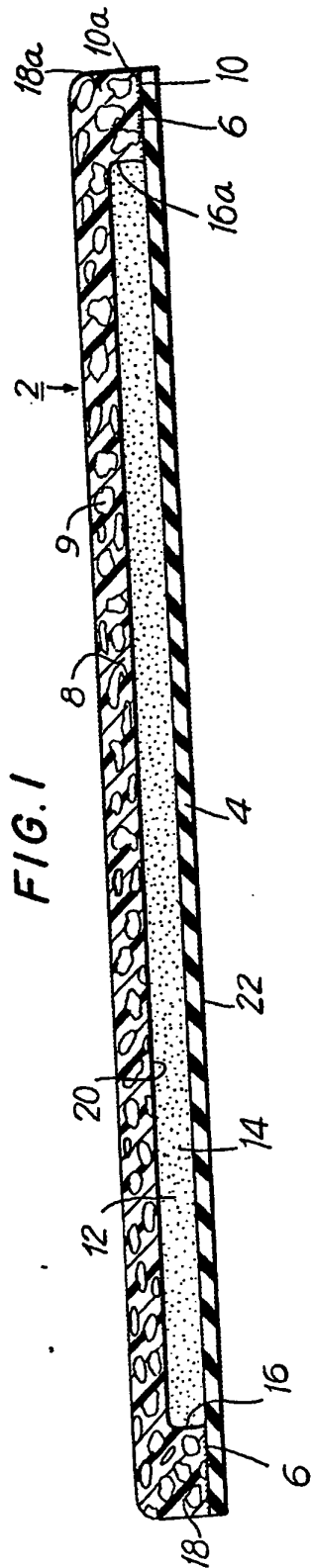
(54) Laundry conditioner dispensing article

(57) This invention relates to a unitary conditioner dispensing article 2

for dispensing conditioning agent in a moving drum laundry machine for containing fabric to be treated. The article comprises a first layer (4) consisting of a magnetised, rubber polymeric material adapted to forcibly, magnetically engage an internal metallic surface portion of the said apparatus in form-retaining relationship therewith, and a second layer (8) attached to or integral with the overlying the said first layer comprising a permeable, sorptive sheet material for containing and dispensing the said conditioning agent.



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## SPECIFICATION

## Laundry conditioner dispensing article

5 The present invention relates in general to a conditioner dispensing article of unitary construction beneficially adapted for repetitive use in an automatic laundry washer, dryer or other circular container of the rotatable drum type and in particular to such an article wherein means for attachment thereof to an inner metal surface of the said container is self-executing thus obviating any necessity for the use of external attachment means.

10 In the laundering of fabric materials such as wool, silk, cotton or synthetics, it is conventional to add one or more conditioning agents at some point in process, for example, in order to impart or enhance softness, or anti-static properties, or resistance to bacteria or to reduce such untoward effects as tangling, wrinkling or knotting. Conditioning agents for such uses are well known. Generally, the agent is added to the last rinse of the wash cycle. However, certain inherent disadvantages have spurred attempts to make feasible the addition of such agents at some point in the laundering process other than the wash cycle. Thus, the presence together in the wash or rinse medium of anionic detergent and cationic material often leads to the formation of unsightly, insoluble precipitates and consequent fabric staining. The tendency severely limits the use of cationic softeners. Addition thereof is necessarily delayed until some point in the laundering process wherein the anionic material is at least substantially depleted. Often, the user is required to attend at least the wash-rinse cycle of the operation in order to add the conditioner at the correct moment. By effecting such treatments in the dryer the foregoing disadvantages are effectively overcome. Moreover, there is no necessity for the conditioning agent to be substantive to the fabrics and to adhere to them strongly in preference to the solvent of the dilute solutions of the wash rinse cycles.

Uniform distribution of the conditioning agent in the dryer whereby to achieve effective contact thereof with the fibrous materials of the washed fabrics in a manner convenient to the user is not however, easily attained. Thus, the use of liquid softener sprays for direction onto the fabrics or, by pretreatment, onto the internal walls of the dryer can be costly. Moreover, the risk of, for example spotting or staining, due to local application of excess conditioning agent may be significant. The use of conditioning articles, generally comprising a base or substrate, which may be form-retaining or flexible, coated and/or impregnated with conditioner provides an improvement. In use, the conditioner is removable to the fabrics but the staining may be severe; for example those stains developed

due to the contacting of cationic conditioning agents, e.g. quaternary ammonium salts, with materials containing colour bodies or heavy metal ions such as ferrous or ferric ion may be removable, if at all, only by dry cleaning.

The use of form-retaining as opposed to flexible bases, to avoid the problems associated with the structural deformations of flexible bases, likewise presents problems, although not difficult to locate by the user, as is the case with flexible conditioning articles, they must nevertheless be removed upon completion of the treatment cycle. Furthermore, they must be of a certain density to prevent them from riding atop the laundry load and thus effectively contacting but a portion of the fabric being treated. Prior art relevant to the foregoing discussion include the following U.S. patents: 3,442,692; 3,632,296; 3,633,538; 3,650,816; 3,676,199; 3,686,025; 3,696,034; 3,698,095; 3,826,682; 3,843,395; 3,895,128; 3,944,494; 3,945,936; 3,947,971; 3,956,556 and 4,098,937.

To overcome the foregoing problems, conditioner articles have been proposed which are equipped with means for their temporary attachment to an inner wall portion of the dryer or washer. In general, the attaching means include clips, and cooperating hook and loop assemblies, e.g. that available commercially in a Velcro fastener, and a variety of other mechanical means. U.S. 3,634,947 describes a conditioner article comprising a base of thin flexible material such as paper or plastics coated on a first side i.e. major surface, with a conditioning agent, waxy in nature and preferably a fabric softener or antistatic agent, and on the opposite side with a pressure sensitive adhesive. The latter enables the article to be attached to the internal wall portion of the dryer apparatus in form-retaining relationship therewith. Expedients of this type avoid to a great extent the problems encountered with articles adapted for commingling with the fabrics. The use of adhesive attachment means involves the risk that bonding strength maybe undermined by the high humidity-high temperature conditions extant in the dryer or washer apparatus. Softening of the adhesive may well occur leading to stripping of the article from the wall portion particularly under the high impact conditions characterizing article-fabric contacting. The article thus becomes commingled with the fabrics. The use of hook and loop means has similar disadvantages since attachment thereof to the wall portion is invariably by adhesive means. To the extent that distortion, e.g. buckling or slippage, of the adhesively attached element occurs, form retaining relationship of the element with the wall portion is not maintained. Such articles are somewhat inconvenient to use since the user must first remove a stripping layer protecting the adhesive. As will be appreciated,

the handling of a necessarily high-track adhesive under laundering conditions can be extremely difficult. Other methods involving some structural modification of the dryer apparatus in order to fixedly engage the conditioner article thereto involve a cost penalty and can be economically prohibitive.

A primary object of the invention is to provide a fabric conditioner article wherein the foregoing and related disadvantages are eliminated or at least mitigated to a substantial extent.

Another object of the invention is to provide such an article wherein any necessity for the use of external means whatever, and a typified by adhesive, clips, hook-loop fastener element and the like to enable attachment of said article, to an internal wall portion of a rotatable drum washer, dryer or equivalent container means for fabrics, is eliminated.

Yet another object of the invention is to provide such an article which may be readily and simply recharged with conditioner by the user upon exhaustion of the prior supply enabling repetitive use of such article.

Still another object of the invention is to provide such an article capable of being attached to an internal wall portion of the dryer, washer or equivalent apparatus by simple hand placement thereof to achieve a stable union of mating surfaces by simple contact thereof, the said union being substantially immune to the ambient conditions such as temperature, humidity or solvent, prevailing in the said apparatus.

A further object of the invention is to provide such an article wherein the disadvantages normally associated with conditioning articles designed for commingling with the fabrics being treated such as flaking off of the conditioner or entrapment of the article, are eliminated.

A still further object of the invention is to provide an apparatus for conditioning fabrics comprising an automatic laundry dryer drum or similar container for laundering fabrics incorporating a conditioner article in accordance with the present invention.

According to the present invention a unitary conditioner article for dispensing conditioning agent in an automatic laundry dryer drum or similar apparatus for containing fabric to be treated, comprises a first layer consisting of a magnetised rubber polymeric material adapted to forcibly, magnetically engage an internal metal surface of the said apparatus in form retaining relationship therewith and a second layer integral with and overlying the said first layer comprising a liquid permeable sorptive sheet material for containing and dispensing the said conditioning agent.

In a further aspect of the invention there is provided an apparatus for conditioning fabrics comprising an automatic laundry dryer drum or similar container for fabric materials, means

for rotating the drum and tumbling fabric materials contained therein, wherein an internal metallic surface portion of the said drum has magnetically attached thereto a conditioner article in accordance with the present invention.

The invention may be put into practice in various ways and three specific embodiments will be described by way of example to illustrate the invention with reference to the accompanying drawings, in which:

Figure 1 is a vertical sectional view of a conditioning article in accordance with a first embodiment of the invention;

Figure 2 is a vertical sectional view of a conditioning article in accordance with a second embodiment of the invention; and

Figure 3 is a vertical sectional view of a conditioning article in accordance with a third embodiment of the invention.

In Fig. 1, a conditioner article in accordance with the invention and generally designated 2 comprises a base sheet 4 of magnetised rubbery polymer (soft rubber) joined by adhesive 6 (e.g. a pressure sensitive or hot melt adhesive) to a sorptive porous top sheet 8 having pores 9, e.g. a polyurethane foam of the open, intercommunicating cell type. The rubbery polymer layer 4 and the top sheet 8 are bonded along their peripheral mating surface portions 10 and 10a respectively, to define a substantially centrally disposed free space volume 12, i.e. providing a reservoir illustrated as containing a conditioner 14. The reservoir 12 is bounded by internal sidewalls 16 and 16a of downwardly extending peripheral portions 18 and 18a and inner surface 20 of the top layer 8. The generally inverted U-shaped configuration of the top layer 8 is given for purposes of more clearly defining the reservoir 12 for receiving the conditioner 14; the reservoir may instead be defined by a substantially planar sheet material, i.e. devoid of end portions 18 and 18a, bonded to the layer 4 as described and slightly oversized with reference thereto to allow accommodation of conditioner 14. In addition to being effective with liquid conditioning agents, the embodiment of Fig. 1 is also useful for the containment and dispensing of solid or semi-solid conditioner materials which become molten under the temperatures prevailing in the dryer and in such form permeate through the porous outer layer 8.

In accordance with the present invention, the layer 4 comprises a rubbery, polymeric sheet material magnetised by the inclusion of magnetic material therein, e.g. a bar magnet or dispersed, magnetised particles. The latter may be substantially uniformly dispersed through out the layer 4 or in such manner as to provide a greater concentration thereof in the outer portions, i.e. in the immediate vicinity of the outer surface 22 of the layer 4. This insures a strong metallic bond as between the

surface 22 and an inner metallic wall portion of the dryer, when the two are mutually contacted, which is sufficient to hold the conditioner article 2 in place throughout the fabric treatment and thereafter as desired. The rubbery polymeric material of the layer 4 is preferably of the soft rubber type and thus sufficiently flexible or pliant to be conformed to and fit tightly against the mating surface portion of the dryer, i.e. in form retaining relationship therewith. These materials are well known in the art and preferably include natural rubbers and synthetic polymeric rubbers derived from homo-polymers and interpolymers of mono- and polyolefins, e.g. ethylene, propylene or butadiene. Hydrocarbon rubbers are ordinarily preferred being of an inert character. The rubber selected should, of course, be immune to the effects of the solvent medium present in the dryer at the temperature prevailing therein.

The material of the outer layer 8 may be flexible or form retaining; in the latter case, the layer should be about the same as that of the layer 4 to enable it to "follow" the contour conformation of the layer 4 without risk of rupture of other form of structural breakdown. The material selected should be permeable to the fluidised form of the conditioner 14 and be absorptive therefor. Suitable materials of the form retaining type are described for example in U.S. 3,634,947 and include, without necessary limitation, synthetic organic polymeric plastics preferably in foam form to provide porosity, e.g. the above mentioned polyurethane, polyvinyl chloride, polystyrene, foamed polystyrene, e.g. of open cell type, glass reinforced polyester, synthetic sponges, and cellulose products including paperboard, or corrugated paper, paperboard or cardboard.

Flexible materials useful for the outer sorptive layer 8 are also described in U.S. 3,634,947 and include papers, plastics, rubbers, cloth sponges, fibres, felts and non-woven fabrics. The fibrous materials may be natural or synthetic. Resilient foamed plastics of the polyurethane type are particularly useful.

The thickness of the magnetised layer 4 and the sorptive layer 8 may vary within the range of from about 0.001 to 10 cm. Generally, the rubbery layer 4 varies within the higher portion of the range stated and is usually from about 0.1 to 10 cm in thickness. The thickness of layer 8 depends for example, upon its sorptive capacity and permeability, i.e. in general the lower the permeability, the less the thickness. Thus, the thickness of the layer 8 may be quite small or conversely, if highly porous as illustrated, at least equal in thickness to the rubbery layer 4, as depicted in Fig. 1.

In the second embodiment illustrated in Fig. 2, a conditioner article, generally designated

24, comprises a magnetised rubbery base layer or sheet 4 and an outer continuous, reticulated sponge layer 26, having pores 28, the sponge layer being adhesively bonded to the base layer 4 by adhesive means 6. This embodiment is useful with solid, a semi-solid as well as liquid forms of conditioning agent. The sponge layer 26 may be substantially form-retaining or may be flexible provided that the impact forces incident thereupon when in place in the dryer, due to contact with the tumbling fabrics, suffice to force the conditioner out from the sponge layer 26 and into contact with the fabrics. Particulate forms of solid or semi-solid conditioner are effectively used in this embodiment and can be incorporated into the layer 26 in molten, liquid or solvent solution from e.g. by spraying, pouring or dropping, such liquid forms onto the layer so as to substantially impregnate the layer, and which are then allowed to dry to solid or semi-solid form. Under dryer temperature conditions, the conditioner melts and in such form is released from the layer 26. Alternatively, solid or semi-solid conditioners can be grated, e.g. by rubbing them on the layer 26 and in such form become trapped within the pores 28 of the layer 26. The sponge material may be natural or synthetic, the latter type affording more control over flexibility.

The embodiment of Fig. 3 illustrates a conditioner article 30 comprising a sorptive, liquid permeable, continuous layer 32, having an extremely fine pore size and a rubbery, magnetised base layer 4.

This embodiment is particularly useful with liquid conditioners although solid and semi-solid types may be incorporated in the layer 32 in a similar manner to that described in connection with Fig. 2. The layer 32 can be fabricated from the materials previously described, e.g. paper or plastics, the essential criteria being that the material selected have an absorptive nature and be permeable to liquid forms of the conditioner which thus impregnate the layer. An adhesive 6 is also used here for bonding the layers together.

The thickness of the layers in the Fig. 2 and Fig. 3 embodiments may vary as described in connection with Fig. 1. The outer sorptive layer of the Fig. 2 and 3 embodiments is usually controlled as to thickness and sorptive capacity so as to contain, upon substantial impregnation thereof, conditioner amounts approximately equal to those required for the conditioning treatment of a single batch of laundry. Amounts in significant excess thereof are generally not recommended in order to avoid the possibility of staining due to the presence of an excess quantity of conditioner. Moreover, since the conditioner may be expensive, it is imperative that waste be minimised. Relatively thin sorptive layers additionally ensure that most of the conditioner is

dispensed during the early part of the drying cycle which ordinarily is preferred.

- According to another embodiment of the invention which is particularly applicable to the embodiments of Figs. 2 and 3, the outer layers 26 and 32 respectively may have applied thereto a magnetised rubbery layer similar to layer 4 but having a discontinuous surface to permit containment/dispensing of the conditioner. The term discontinuous is used to mean that such a layer is such as to expose the conditioner to the effects of the laundering medium, be it in the washer, dryer or other similar apparatus. The discontinuity may be perforate or otherwise.

- The use of an absorbent (sorptive) material for containing and dispensing the conditioner in accordance with the invention is essential. The term "absorbent" or "sorptive" as used herein is intended to connote materials of the type described, which are capable of taking up and retaining at least 3 and preferably up to about 50 times, preferably from about 5 to 25 times, and more preferably from 5 to 15 times their own weight of water. Determination of sorptive capacity can be in accordance with the procedure given in U.S. 3,843,395 which modifies the capacity testing procedures described in U.S. Standard Specification UU-T-595b. Pore size may range from exceedingly fine, e.g. 100 to 200 pores per inch (Fig. 3) to relatively large, e.g. 10 to 20 pores per inch (Figs. 1 and 2). In either case, it is required that the materials have a relatively high percentage of void volume or free space, i.e. at least about 40% and preferably 50% up to about 90% of the total volume of the sorptive layer is free space. Materials having the larger pore size (Figs. 1 and 2) are more effective for containing solid and semi-solid conditioner agents and particularly when applied to the layer in solid form as by merely rubbing the solid conditioner there against to "grate" the conditioner. The resultant particles become entrapped within the porous structure. Thus, according to the invention, permeation of impregnation rather than coating of the sorptive layer is achieved.

- In use, the conditioner article herein is merely handplaced against an internal metallic wall portion of the dryer apparatus such as the rotatable drum, door, fin or baffle. Although normally attached intermediate the baffles, it is often preferred to mount the conditioner article on the baffles or other raised portions of the interior of the drying drum. Generally, this will be on a leading edge so as to promote optimum contact with the fabrics being conditioned. In any event, experience will aid in selecting the most effective locations for article attachment.

- Usually, the article as commercially supplied will contain the conditioner. If not, it may be added to the sorptive layer in the manner previously described, e.g. by spray-

- ing, pouring, dropping or rubbing. The dryer, after loading with washed fabric is activated causing relative movement between the conditioner article and laundry. The combination of heat, moisture and impact contact between the article and the laundry effect the release of conditioner through the sorptive layer onto the tumbling fabric. Although the conditioning treatment is preferably carried out in the laundry dry dryer, other laundry tumbling apparatus such as the washing machine may be used. Moreover, heat and drying air may be omitted for part or all of the cycle. Ordinarily, there will be about 5 to 50 changes of drying gas in the dryer drum per minute and the gas temperature will be from about 10 to 90°C and preferably from 50 to 80°C. The drum rotates at about 20 to 100 and preferably 4 to 80 revolutions per minute. The laundry load usually averages from 4 to 12 pounds and will occupy from 10 to 70% of the effective drying volume of the dryer. Drying generally takes from 5 minutes to 2 hours and usually from 20 to 60 minutes. Synthetic fabrics such as nylon and polyester ordinarily require only 3 to 10 minutes while permanent press materials usually require from 10 to 30 minutes.

- The conditioner article, after use, may be left in place and re-charged when necessary with a selected amount of conditioner prior to subsequent use in the manner described. Since the magnetically bonded article is strongly affixed to the internal wall portion there is little, if any, danger of unseating the conditioner article as a result of the re-charging operation, even if such requires abrading contact of the conditioner with the sorptive layer of the article. Alternatively, the article may be removed by hand with the exertion of but slight pulling force exerted substantially normally to the plane of the major surface of the sorptive layer. However, re-charging does not require removal of the article. The conditioner article, can of course, be relocated as desired in the washer or dryer, as the case may be, at the sole option of the user. As a further option, a plurality of articles may be positioned within the apparatus to achieve diverse conditioning effects in a single operation.

- Conditioning agents useful herein include fabric softeners and antistatic agents including nonionic surface material, e.g. high fatty acid monolower alkanolamides, higher fatty acid dilower alkanolamides, block copolymers of ethylene oxide and propylene oxide having hydrophilic and lyophobic end groups, alkyl (preferably middle alkyl) phenol polylower alkylene oxide lower alkanols, polymers of lower alkylene glycols, polyalkylene glycol ethers of higher fatty alcohols and poly alkylene glycol esters of higher fatty acids. Among the anionic agents are the higher fatty acid products with water soluble bases, higher fatty alcohol

5 sulphates, higher fatty acid monoglyceride sul-  
phates, sarcosides and taurides and linear  
higher alkaryl sulphonates. Cationic com-  
pounds include the higher alkyl, dilower alkyl  
5 amines, dihigher alkyl, lower alkyl amines and  
quaternary compounds, especially quaternary  
ammonium salts, e.g. quaternary ammonium  
halides. "Lower" as used herein means C<sub>1</sub>-C<sub>8</sub>  
alkyl and preferably C<sub>2</sub>-C<sub>3</sub>. The term "higher"  
10 means C<sub>10</sub>-C<sub>20</sub> and preferably C<sub>12</sub>-C<sub>18</sub>. Mix-  
tures of nonionic conditioning agents with cat-  
ionic or anionic agents of the types mentioned  
above may also be used and generally the  
proportions of the components of such mix-  
15 tures will be chosen so as to have the final  
product in liquid or solid or semi-solid form as  
desired and such as to be satisfactorily remo-  
vable by a combination of moisture, heat and  
impact contact with the laundry in an auto-  
20 matic dryer.

Specific examples of surface active materi-  
als of the type described above are given in  
the book "Synthetic Detergents" by  
Schwartz, Perry and Berch, published in 1958  
25 by Interscience Publishers, New York, see  
pages 25 to 143. Among the more preferred  
of these are:

Nonionic — nonylphenoxy polyethoxy ethan-  
ol, stearic monoethanolamide; stearic di-  
30 ethanolamide; block copolymers of ethylene  
oxide and propylene oxide (Pluronic);  
Anionic — sodium soap of mixed coconut  
oil and tallow fatty acids; sodium stearate;  
potassium stearate; sodium laurate; tallow  
35 alcohols sulphate;  
Cationic — dilauryl dimethyl quaternary  
ammonium chloride; hydrogenated tallow  
alkyl trimethyl ammonium bromide and  
benzethonium chloride.  
40 Amphoteric — e.g. cocoamido betaines,  
and mixtures of the foregoing.

The above list is only illustrative of some of  
the compounds useful in accordance with the  
present invention. Conditioning agents of  
45 these types are well known in the art and  
others than those mentioned above may also  
be used satisfactorily.

In addition to the fabric softener and or  
antistatic and unwrinkling agents which are  
50 the principal conditioning compounds, other  
components may also be present in these  
conditioning compositions for their adjuvant  
effects. Thus, other conditioning agents may  
be used, including those designed to treat the  
55 fabrics in other ways than in softening. For  
example, perfumes, brighteners, bactericides,  
solvents, thickening or hardening agents, sta-  
bilizers and other materials may be incorpo-  
rated in the conditioning compositions. In  
60 some cases, small quantities of water may be  
present, especially when the components form  
hydrates. Solvents and dispersants may be  
used to assist in applying the conditioner  
compositions to the sorptive layer being  
65 coated with the conditioning composition. The

types and proportion of the various adjuvants  
used will be chosen to make them non-inter-  
fering with the operations of the conditioning  
compounds.

70 The following examples are given for pur-  
poses of illustration only and are not intended  
to limit the invention. Parts are by weight  
unless otherwise indicated.

#### 75 EXAMPLE 1

A mixture of (A) 65 parts of a 1:1 mixture  
of distearyl dimethyl ammonium chloride and  
cocoamide propyl betaine and (B) 35 parts of  
tallow monoethanolamide were mixed and  
80 melted together; then cast into a bar of 20  
grams. The bar was placed centrally on a  
Plastiform rubber magnet sheet (leaving a  
peripheral edge). This material is made from  
an ethylene-propylene rubber loaded with  
85 65% by weight of barium ferrite. A sheet of  
1:1 to cotton: Dracon 117 × 50 threads/in.  
weighing 5.5 oz/sq. yd. was laid over the bar  
and rubber sheet were heat sealed to each  
other around their edges. The conditioner can  
90 wick through the fabric to the surface by  
capillary action. When this assembly  
(2½" × 4") was attached by the magnetic  
rubber sheet to a dryer wall it was found that  
the product was satisfactory for 40 dryer  
95 cycles and gives excellent softness and anti  
static qualities to clothes dried in those 40  
treatments.

#### EXAMPLE 2

100 Example 1 was repeated using 20g in bar  
form of the following composition:  
(A) 80/20 dimethyl distearyl ammonium  
methyl sulphate/cocoamidopropyl betaine;  
(B) dimethyl distearyl ammonium chloride.  
105 Similar excellent results are obtained.

#### EXAMPLE 3

A 4" × 4" × 5/8" cellulose sponge was  
adhesively secured around its edge to a  
110 4" × 4" Plastiform rubber magnet sheet. The  
sponge was then impregnated with 30 grams  
of a 6% aqueous solution of dimethyl dis-  
tearyl ammonium chloride. The composite was  
attached to a dryer wall and gave excellent  
115 softening of a 9 lb load of laundry dried  
therein. After 1 cycle there was still a fair  
amount of softener in the sponge. The sponge  
assembly can be removed and reimpregnated  
as desired and necessary for repeated usage.

#### 120 CLAIMS

1. A unitary conditioner article for dis-  
pensing conditioning agent in a moving drum  
laundry machine for containing fabric to be  
125 treated comprising a first layer consisting of a  
magnetised, rubber polymeric material  
adapted to forcibly, magnetically engage an  
internal metallic surface portion of the said  
apparatus in form-retaining relationship  
130 therewith, and a second layer attached to or

integral with and overlying the said first layer comprising a permeable, sorptive sheet material for containing and dispensing the said conditioning agent.

- 5     2. An article as claimed in Claim 1, in which the said first and second layer are continuously joined along the peripheral portions thereof to define an enclosed free space, reservoir portion therebetween for receiving
- 10 the said conditioner.

3. An article as claimed in Claim 1 or Claim 2, in which the said second layer is a form-retaining, polyurethane foam.

- 15     4. An article as claimed in Claim 3, in which the foam is an open cell foam.

5. An article as claimed in any one of Claims 1 to 4, in which the said first and second layers are adhesively bonded together at their points of contact.

- 20     6. An article as claimed in any one of Claims 1 to 5, impregnated with a conditioner selected from solid, semi-solid and/or liquid softeners, antistatic agents, brighteners, bleaching agents, bacteriostats and perfumes.

- 25     7. An article as claimed in any one of Claims 1 to 6, in which the said rubbery polymer material is selected from natural rubber and homo- and interpolymers of mono- and poly-saturated hydrocarbon monomers,
- 30 the polymeric material having the flex and form-retaining properties of soft rubber.

8. An article as claimed in Claim 7, in which the said rubbery, polymeric material is a copolymer of styrene and butadiene.

- 35     9. An article as claimed in any one of Claims 1 to 8, in which the said second layer is selected from natural and synthetic sponges, foam sheet, paper, cloth, and porous film forming organic polymeric materials, of
- 40 the form retaining or flexible type.

10. An article as claimed in Claim 9, in which the said second layer comprises reticulated sponge.

11. An article as claimed in Claim 1,
- 45 substantially as specifically described herein with reference to Fig. 1, 2 or 3.